Supplementary information for

Laser-driven phase transitions in aqueous colloidal gold nanoparticles under high pressure: Picosecond pump-probe study.

Shuichi Hashimoto,†* Tetsuro Katayama,‡ Kenji Setoura,† Michael Strasser,†
Takayuki Uwada,‡ and Hiroshi Miyasaka†*

† Department of Optical Science and Technology, University of Tokushima, 2-1 Minami-Josanjima,
Tokushima, Tokushima 770-8506, Japan,

‡ Division of Frontier Materials Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka
560-8531, Japan,

‡ Department of Chemistry, Josai University, 1-1 Keyakidai, Sakado, Saitama 351-0295, Japan.

*Corresponding author E-mail: hashichem@tokushima-u.ac.jp, miyasaka@chem.es.osaka-u.ac.jp
S1. Two-temperature model

Coupled TTM equations in the NP-medium systems are given by:

\[
C_e(T_e) \frac{dT_e}{dt} = -g(T_e) \cdot (T_e - T_L) + S(t), \quad (S1)
\]

\[
C_i(T_i) \frac{dT_i}{dt} = g(T_e) \cdot (T_e - T_L) - F, \quad (S2)
\]

\[
C_m(T_m) \frac{\partial T_m}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( k_m(T_m) r^2 \frac{\partial T_m}{\partial r} \right). \quad (S3)
\]

Here \( C \) denotes the heat capacity, \( g(T_e) \) is the electron-phonon coupling constant, \( k \) is the thermal conductivity, \( S \) is the energy input to the free electrons by the laser pulse, and \( F \) is the heat loss at the NP-water interface. The indices \( e, L \) and \( m \) represent the electron, lattice, and medium. The energy deposition term is described by:

\[
S(t) = C_{abs}(\lambda) \cdot \frac{P(t)}{V} \quad (S4)
\]

where \( C_{abs} \) is the absorption cross-section of an AuNP, \( P(t) \) is the time-dependent laser power density, and \( V \) is the particle volume. One can describe \( P(t) \) in the center of the Gaussian power distribution by:

\[
P(t) = \frac{2 \sqrt{\ln(2)}}{\sqrt{\pi} \cdot \tau_p} \cdot I \cdot \exp \left( -\frac{4 \ln(2)}{\tau_p^2} t^2 \right) \quad (S5)
\]

Here, the power density function is defined by the pulse duration \( \tau_p \) (FWHM) and laser fluence \( I \). The heat loss term \( F \) was given by Plech and co-workers\(^1\) by introducing an interfacial thermal conductance \( G \), experimentally determined as 105 MW m\(^{-2}\) K\(^{-1}\) for small AuNPs of 35 nm diameter in aqueous solution. The implication of \( G \) is given by the surface wetting of nanoscale objects. The heat loss term, \( F \) in eq. S2 is given by

\[
F = 3 \frac{G}{r} (T_e - T_m) \quad (S6)
\]
The heat loss term is determined by the temperature gradient of $T_L$ and the medium temperature at the NP-water interface $T_m (r)$, with $r$ being the NP radius. The temperature dependent-conductance parameter is given by: \[ G = \frac{3C_m k_m}{rC_L} \] (S7)

where $C_m$ is the heat capacity of the medium water, $k_m$ is the thermal conductivity of water, $r$ is the particle radius, and the $C_L$ is the heat capacity of particle. Here the factor 3 and $r$ originate from the ratio of surface to volume. Furthermore, in the solid state the linear thermal expansion coefficient $\alpha$ of Au is given by $1.24135 \times 10^{-5} + 5.0786 \times 10^{-9} T_L$. For the liquid state, on the other hand, no thermal expansion coefficients were found, thus Koike’s experimentally determined density $\rho_{Au} (T_L) = 1.74 \times 10^4 - 1.44 (T_L - 1336)$ was applied. It is known that the volume of Au increases of approximately 3.8 % due to the phase transition from solid to liquid, which is in good agreement with the above function. As results are based on experiments performed in vacuum and atmospheric pressure, one can assume that the behavior may differ for AuNPs under high pressures. Moreover, we assume that thermal expansion stops at the bp of Au. The electron-phonon coupling constant $g$ and electron heat capacity $C_e$ were adopted from the calculations of Lin and co-workers, based on the real electron density of state (DOS) instead of the frequently used linear FEG model. For temperatures sufficiently above the Debye temperature, the specific heat capacity of gold can be calculated by $C_L(T_L) = (119 + 3.061 \times 10^{-2} T_L)$ in the solid phase and is assumed to reach a value of 149 J kg$^{-1}$ K$^{-1}$ in the liquid phase. At high pressures, physical properties of water such as refractive index, thermal conductivity, density and heat capacity are accurately known at limited temperatures. For temperatures above 800 K and 2000 K, where the temperature at the NP-water interface exceeds the area of experimental accuracy, the parameters were fitted or assumed as constant.
S2. Temperature-dependent extinction spectra of Au NP.

Fig. S1. Temperature-dependent extinction spectra for 60-nm diameter Au NP in water (n: 1.33) simulated using Mie theory.
S3. Transient extinction signal at 532 nm as a function of time exceeding 6 ns.

![Graph showing transient extinction signal at 532 nm](image)

**Fig. S2** Extinction change observed at 532 nm when excited by a 355 nm, 15 ps laser with a fluence of 19.6 mJ cm$^{-2}$ under a pressure of 60 MPa (probe light: CW laser (PHOTOP, DPGL-2050F), detector: photodiode (Thorlabs, DET10A/M, rise time < 1 ns)) at a time scale longer than that of the pump-probe measurement, showing the indication of permanent bleach. The extinction signals were 19-times accumulated. The permanent bleach was not observed at 4.5 mJ cm$^{-2}$.
S4. Effect of G value on $T_e$, $T_L$, and $T_m$.

G: 20 MW m$^{-2}$ K$^{-1}$

G: 60 MW m$^{-2}$ K$^{-1}$

G: 100 MW m$^{-2}$ K$^{-1}$

G: eq. S7

Fig. S3  TTM-based simulation of temporal behavior of $T_e$, $T_L$, and $T_m$ for various G values for 60-nm diameter AuNP in water when excited with a 15-ps FWHM pulsed laser (excitation wavelength: 355 nm) at a fluence of 10 mJ cm$^{-2}$. 
S5. Simulated transient extinction spectra for various thicknesses of supercritical layer.

![Graph](image)

**Fig. S4**  (a) Simulated transient extinction cross-section ($\Delta C_{\text{ext}}$) spectra for a AuNP/supercritical layer/water structure in which a spherical 60-nm diameter AuNP, surrounded by various thicknesses (given in numbers in the figure) of a concentric spherical supercritical layer (refractive index: 1.1), is submerged in water (refractive index: 1.34). The AuNP was assumed to be a liquid droplet ($T_L > 1336$ K). Each transient spectrum was obtained by subtracting a spectrum at room temperature in water from the original extinction spectrum formed by laser irradiation.
(b) Simulated supercritical layer thickness vs. difference extinction cross-section value ($\Delta C_{\text{ext}}$) for a single 60-nm diameter AuNP at four wavelengths: 470, 490, 525, 600 nm.
S6. Laser-induced size reduction at 0.1 MPa.

**Fig. S5** Particle image (TEM photograph) and corresponding size distribution for 60-nm-diameter AuNPs excited with a 15-ps FWHM pulsed laser (excitation wavelength: 355 nm) for 5000 shots at a fluence of 20 mJ cm\(^{-2}\).
References

5. F. C. Nix and D. MacNair, Phys. Rev. 1941, 60, 597.